

Liquid Transport Through Membranes Prepared by Grafting of Polar Monomers onto Poly(tetrafluoroethylene) Films. I. Some Fractionations of Liquid Mixtures by Pervaporation

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Synopsis

The separation of various liquid mixtures including systems of chloroform-hydrocarbons or ethyl ether, water-alcohols and water-nucleophilic organic solvents have been investigated by the pervaporation technique. Membranes were obtained by grafting Lewis base onto poly(tetrafluoroethylene) (PTFE) films. The PTFE backbone has been chosen for its mechanical and chemical resistance. N-Vinylpyrrolidone and 4-vinylpyridine were selected because of their great affinity for the electrophilic compounds. In all cases, the compound which has the greatest affinity for the membrane pervaporates selectively through modified PTFE films. Selectivity and rates were studied. It is concluded that because selectivity is very important, total separation of different mixtures is possible at a good yield, with a faster rate when the temperature is increased or the thickness of the membrane is decreased.

INTRODUCTION

Pervaporation

Fractionation of liquid mixtures by selective transport through polymer membranes may be achieved by using three different techniques: vapor permeation, ultrafiltration, or pervaporation.

In vapor permeation techniques (vapor-vapor transport), the polymer membrane is in contact with the vaporous mixture in equilibrium with the liquid mixture. The diffusing species are removed from the opposite side as vapor.

Ultrafiltration (liquid-liquid transport) is a widely used technique for water desalination. This process depends on applying pressure to the liquid mixture and driving the liquid through the membrane.

In the pervaporation process (liquid-vapor transport), the membrane is brought in contact with the liquid mixture at atmospheric pressure, and the liquids permeate into the membrane to vaporize downstream. Down-

stream of the membrane, vaporization is achieved by maintaining a low vapor pressure through a vacuum pump or an inert gas flow.

The earliest work on fractionating liquid mixtures by pervaporation technique was developed in the mid-1950's.^{1,2} This process is potentially useful in fields where distillation techniques are difficult, such as fractionation of close-boiling components, azeotropic mixtures, or isomeric mixtures.²⁻⁸ Other applications can include the separation of heat-sensitive mixtures, the concentration of fruit juices,⁹ the elimination of impurity traces, or the removal of water from an esterification reaction as soon as it is formed.¹⁰ Different papers can be consulted for a more comprehensive survey of the field.¹¹⁻¹⁶

Membrane and Molecular Interactions

We are not yet in a position to describe the pervaporation mechanism exactly. We can only say that this process consists of dissolution of the species into the membrane, diffusion through it, and evaporation at the downstream side. We also know that the rate and the selectivity of the transfer are governed by a great number of factors, including all the physico-chemical properties of the polymer or the liquid mixtures and other factors such as temperature, pressure, and membrane thickness.

Research on pervaporation to date has neglected to emphasize the role of the interactions between the diffusing species and the polymer. The main reason for this is that the membranes used for pervaporation studies were manufactured commercially for other membrane applications. These membranes can be classed into two categories according to the type of the generating polymer: chemically inert membranes and polar membranes.

The chemically inert membranes are prepared from polyolefins (polyethylene or polypropylene) or from polymers the repetitive unit of which is symmetrical (poly(tetrafluorethylene)). They possess the property of remaining inert in organic or inorganic media. Thus the governing parameters of pervaporation rate and selectivity are related more closely to physical factors such as molecular size and shape of the diffusing species or membrane structure than to polarities or other chemical properties.¹⁷⁻¹⁹

The polar membranes are prepared from polar polymers (polyalcohols, polyamides, polyethers, polyesters, etc.). The most widely used are cellulose acetate, modified cellulose, and nylon membranes. Such membranes largely interact with polar species of a liquid mixture; the interactions are more or less strong according to the species and consequently may control the selectivity of the pervaporation.¹²

Lewis Polybases

Among the polar polymers, a particular place must be assigned to Lewis polybases which are polymers with a repetitive unit possessing proton-acceptor groups but not proton donor groups (ether, ester, carbonyl, N-disubstituted amide groups). Thus the nucleophilic groups are not intramolecular hydrogen-bonded groups; they keep their entire proton-acceptor

force toward outside electrophilic molecules. When such a polymer is used in pervaporation experiments, specific interactions take place between the active groups of the membrane and the electrophilic species, and it is to be expected that these specific interactions will control the pervaporation rate of such compounds. Indeed, through a polymorpholide acrylic or a polypyrrolidide acrylic membrane, the faster vapor permeation rate is obtained with the compound which is strongly H-bonded with the polymer basic units.^{20,21}

The disadvantage of such membranes is their solubility in many organic solvents and their insufficient mechanical resistance. These defects can be removed by using a copolymer composed of a Lewis-base monomer and another monomer; the latter must confer its superior chemical and mechanical properties to the synthesized copolymer.

In this present study, good results were obtained by grafting Lewis bases onto poly(tetrafluoroethylene) films (PTFE films). The PTFE backbone has been chosen because of its particularly good qualities. N-Vinylpyrrolidone (VP) and 4-vinylpyridine (4VP) were selected because of their easy grafting onto PTFE films and their known strong affinity for electrophilic compounds.

This paper is concerned with the first results obtained in pervaporation with such membranes and various mixtures.

EXPERIMENTAL

Apparatus

The apparatus for measuring pervaporation through modified PTFE films is shown in Figure 1, and a cross section showing details of the pervaporation cell is given in Figure 2.

The pervaporation cell was made of stainless steel. The membrane M, supported on a sintered stainless steel disc F, separated the cell into two compartments. A Teflon or Viton gasket J was placed on the membrane, and the two compartments were packed together by means of six coupling bolts G and nuts E.

The upper compartment had a capacity of about 110 ml, and the membrane area in contact with the liquid was 20 cm². It was provided with a heating jacket T in which a water flow at controlled temperature was established by means of a sensitive thermostat. A thermometer was placed into the thermowell W, and a reflux condenser on R.

Vigorous agitation of the liquid contents was provided by means of a circulation pump (Fig. 2); the liquid flowed into and out of the upper compartment by two outlets A placed symmetrically just above the surface of the membrane.

The outlet joint S₂ from the lower compartment was connected to traps cooled by liquid air. A vacuum of 10⁻³ mm Hg was maintained by a vacuum pump. Pressure was controlled by a Pirani gauge and a manometer measured pressures above 1 cm Hg.

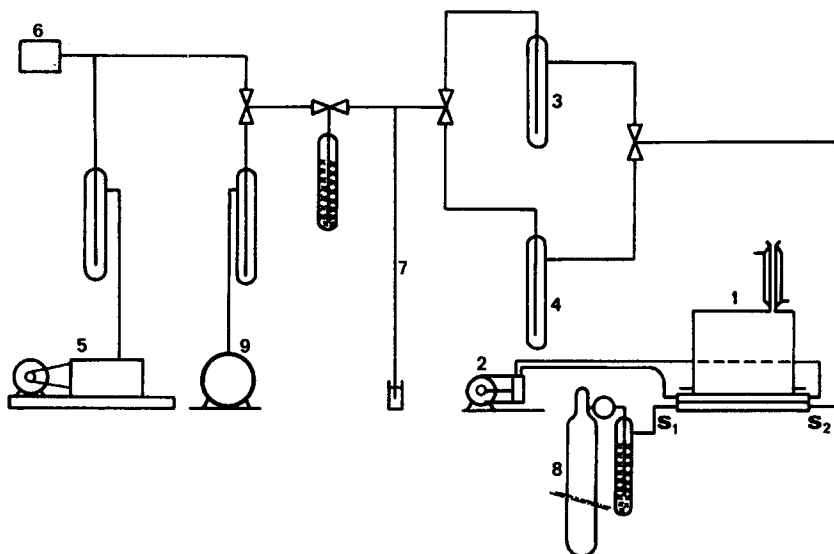


Fig. 1. Experimental apparatus: 1. pervaporation cell, 2. circulation pump, 3 & 4. traps, 5. vacuum pump, 6. Pirani gauge, 7. manometer, 8. nitrogen bottle, 9. flow gauge.

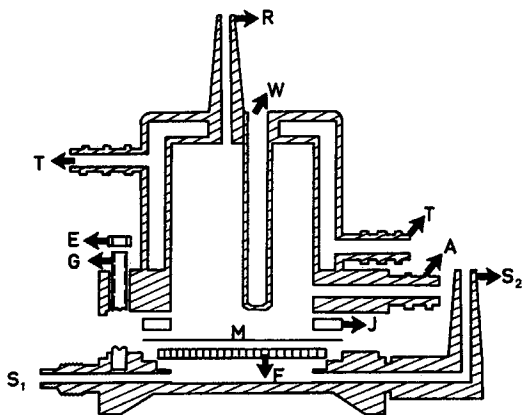


Fig. 2. Pervaporation cell

When an inert gas flow was chosen to remove the pervaporated species, the outlet joint S_1 was connected to a nitrogen bottle and a flow gauge placed behind the cold traps.

Membranes

The poly(tetrafluoroethylene) (PTFE) films were kindly supplied by the Société Ugine-Kuhlmann. The films were of different thicknesses (17μ and 55μ). Asymmetrical films were also used; they were composed of a dense skin 1, 2, or 3μ in thickness and a porous part 14, 13, or 12μ in thickness respectively.

Poly(tetrafluoroethylene)-poly(4-vinylpyridine) grafted membranes (PTFE-P4VP) were prepared by grafting in the bulk of a PTFE film;²² the latter was placed in an ampoule containing a solution of freshly distilled 4-vinylpyridine in methanol. Vacuum-sealed ampoules were exposed to cobalt 60 γ -rays. After irradiation, the membranes were washed and treated with 0.1*N* KOH to ensure that the 4VP groups were in a nonionic state.

The poly(tetrafluoroethylene)-poly(*N*-vinylpyrrolidone) grafted copolymers (PTFE-PVP membranes) were prepared by using a similar technique.²³ In this case the solutions of freshly distilled *N*-vinylpyrrolidone were benzene or pyridine solutions.

The grafting ratio was expressed by the weight ratio

$$\frac{W - W_0}{W_0} \%$$

where *W* is the weight of the grafted membrane and *W*₀ is the weight of the original PTFE films.

Chemicals

All the organic liquids used in the pervaporation process were commercial compounds. They were supplied by Prolabo ("pour analyse" or "technique" quality). The "technique" products were distilled (*N,N*-dimethylacetamide; *N,N*-dimethylformamide), but the others were used without further purification.

Analysis of Binary Mixtures

The composition of the samples collected in the traps was determined with a universal refractometer OPL. In the case of mixtures containing compounds of similar refractive indexes, a Carl Zeiss precision refractometer (precision superior to the fifth decimal) was used.

The low water concentrations were determined by a Karl Fisher apparatus.

Procedure and Representation of Results

In order to express the characteristic behavior of a membrane toward a given liquid mixture, the following conventions were selected.

Suppose a pervaporation test was carried out with a binary system consisting of two liquids A and B (pervaporant). The total volume was *V*, the partial volumes were *V*_A and *V*_B and the volume fractions were *x*_A and *x*_B:

$$x_A = \frac{V_A}{V} \quad x_B = \frac{V_B}{V}$$

The diffusing species (pervaporate) were condensed in a trap. Every hour, this trap was removed from the apparatus and another one was then

connected. The volume v and the composition (volume fractions y_A and y_B) were measured:

$$v = v_A + v_B \quad y_A = \frac{v_A}{v} \quad y_B = \frac{v_B}{v}$$

These values permit the calculation of the volume fraction X of the vaporant and the volume fractions Y_A and Y_B of the two compounds which have been pervaporated since time zero:

$$X = \frac{\Sigma v}{V} \quad Y_A = \frac{\Sigma v_A}{V_A} \quad Y_B = \frac{\Sigma v_B}{V_B}$$

Between X , Y_A , and Y_B the following relation may be easily verified:

$$X = x_A Y_A + x_B Y_B$$

or

$$2X = Y_A + Y_B$$

when the initial mixture is composed of equal volumes of A and B. Graphs of Y_A and Y_B versus X can be plotted. The more the graphs diverge, the better is the fractionation.

The membrane selectivity of a binary system composed of two liquids can be expressed in terms of a selectivity factor α , defined as the concentration ratio y_A/y_B in the pervaporate divided by the ratio x_A/x_B in the vaporant:

$$\alpha = \frac{y_A/y_B}{x_A/x_B}$$

A is the species which is preferentially pervaporated. During the pervaporation, the volume fractions x_A and x_B vary, so α is not constant. Considering α_0 as the selectivity factor at the initial stage of the transfer, it can be easily shown that α_0 is the ratio between the tangent slopes of the two graphs Y_A versus X and Y_B versus X at the origin.

A second important characteristic factor is the pervaporation rate; it will be designated by ϕ and expressed in liters per hour and square meter (l./hr m²). In all the figures and tables, the values of α and ϕ will be taken at the initial stage of the pervaporation. In all the experiments, vaporization of the diffusing species at the downstream side of the membrane has been achieved by maintaining a 10⁻³ mm Hg pressure through a vacuum pump.

RESULTS AND DISCUSSION

Chloroform-Hydrocarbon and Chloroform-Ethyl Ether Mixtures

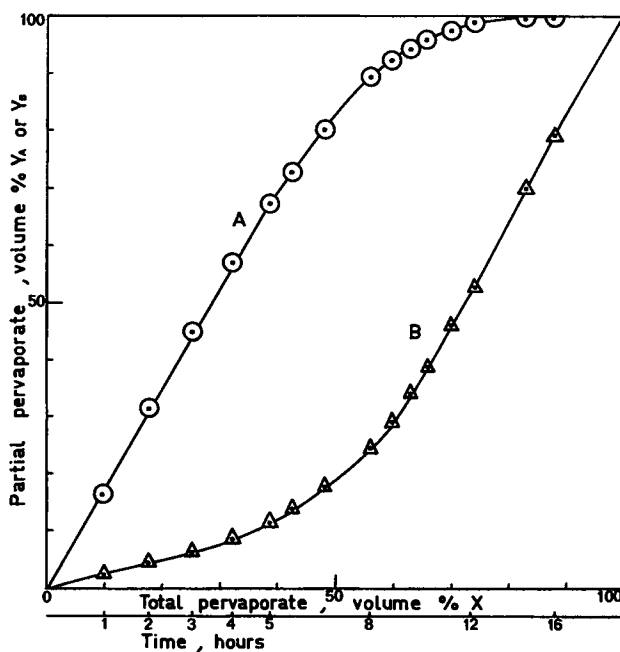
In this part, all the mixtures consisted of chloroform and another compound. Chloroform presents specific interactions with the basic groups

VP or 4VP inside the membranes. Since chloroform is a nonself-associated proton donor solvent, it is able to be bound by H bonds to electron donors, i.e., with the N group of the 4VP units or with the CO group of the VP units.

The other compound of the mixture does not present such specific interactions with the active groups of the membrane, neither has it a solvation effect on the polymer.

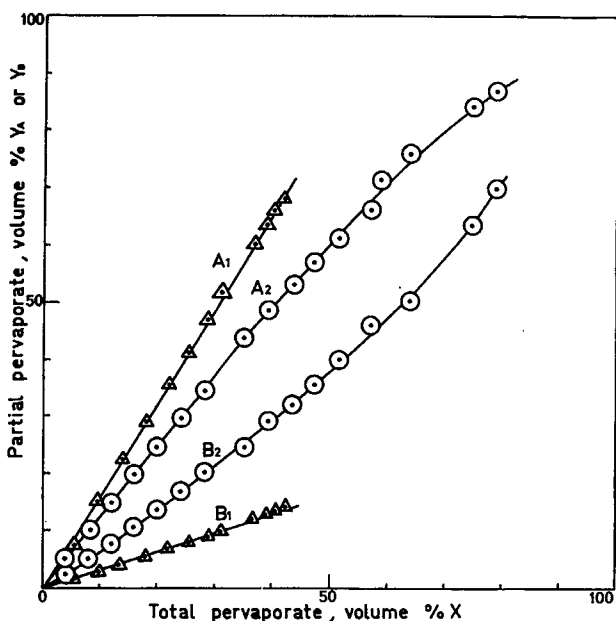
Experimental results are listed in Figures 3-5. In all cases, the proton donor compound, i.e., the species which presents the greatest affinity for the membrane, pervaporates selectively through PTFE-P4VP membranes. This trend agrees with the results obtained with PTFE-PVP or other PVP membranes²⁴ and corresponds to the conclusions of other workers.^{12,19}

The results also indicate that the polar-nonpolar systems (chloroform-hydrocarbons) are more easily separated than the binary systems where the two species are associated by an H bond (chloroform-ethyl ether). Thus, in the former case, at the end of the experiment, the nonpervaporated fraction contains pure hydrocarbon which represents about 60% of its initial volume.



Mixture	Membrane	Temperature	Characteristic factors
A: Chloroform (26.5 ml)	PTFE-P4VP 57% grafting	-20°C	$\phi = 2.5 \text{ l./hr m}^2$
B: Hexane (23.5 ml)	PTFE thickness: 17 μ area: 20 cm ²		$\alpha = 6.7$

Fig. 3. Pervaporation graphical representation.



Mixture	Membrane	Temperature	Characteristic factors
A ₁ : Chloroform (25 ml)	PTFE-P4VP	20°C	$\phi = 3.8$ l./hr m ²
B ₁ : Pentane (25 ml)	57% grafting		$\alpha = 5.1$
A ₂ : Chloroform (25 ml)	PTFE thickness: 17 μ	20°C	$\phi = 0.95$ l./hr m ²
B ₂ : Ethylether (25 ml)	area: 20 cm ²		$\alpha = 2.0$

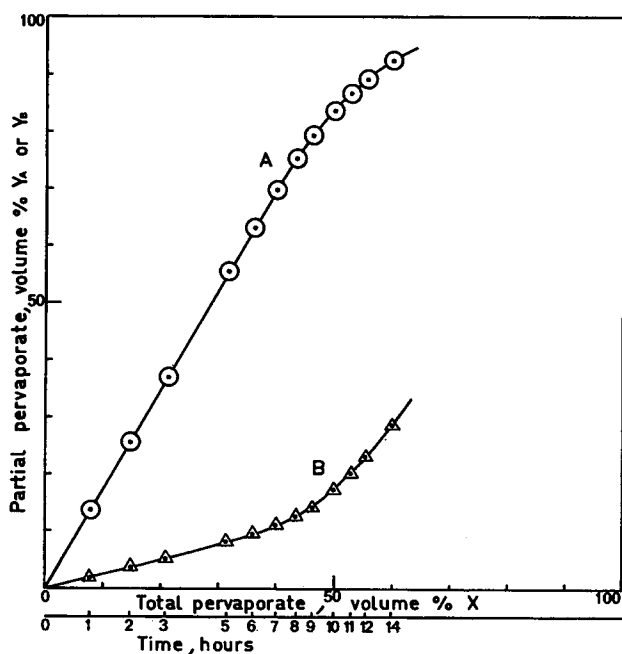
Fig. 4. Pervaporation graphical representation.

The azeotropic chloroform-hexane mixture (Fig. 3) is separated with the same facility as the others: when the binary mixture of azeotropic composition (53 vol-% chloroform) is studied, the nonpervaporated fraction is found to be highly enriched with hexane, and in spite of the azeotropic composition, selectivity and rate are not affected. This is also the case when the other compound of the mixture has a lower boiling point than chloroform (Fig. 4).

Alcohol-Water Mixtures

Alcohol-water mixtures were extensively investigated in order to obtain pure alcohol by a more economic process than the usual ones. For alcohols containing a maximum of 0.7% water (just saleable), pervaporation has been claimed as very efficient.^{1,2}

Experimental graphs Y_A and Y_B versus X are shown in Figure 6. With an initial solution composed of 96 ml ethanol and 4 ml water pervaporating through a PTFE-P4VP membrane (195% grafting, 20 cm² area) at 60°C,



Mixture	Membrane	Temperature	Characteristic factors
A: Chloroform (25 ml)	PTFE-P4VP 57% grafting	20°C	$\alpha = 6.5$
B: Cyclohexane (25 ml)	PTFE thickness: 17 μ area: 20 cm ²		$\phi = 1.8 \text{ l./hr m}^2$

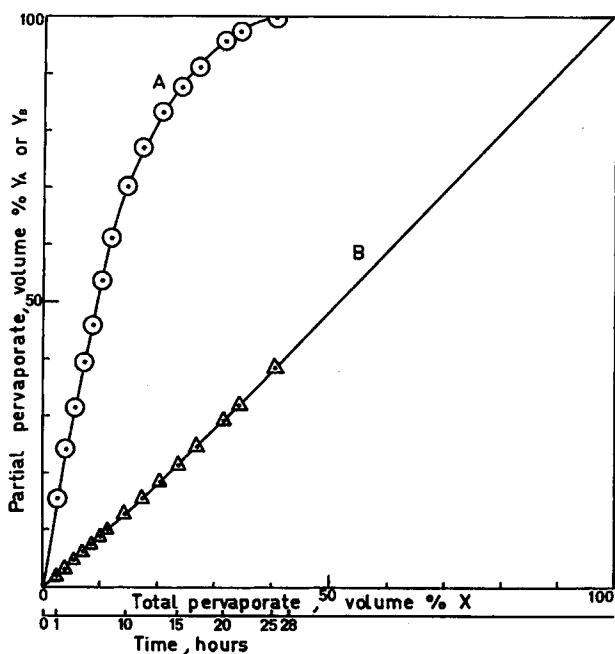
Fig. 5. Pervaporation graphical representation.

approximately 60 ml of a nonpervaporated fraction consisting of at least 99.7 vol-% ethanol was obtained over a period of about 30 hr.

In the case of an azeotropic ethanol-water mixture (3.5 vol-% water), modified PTFE membranes were compared with commercial membranes (Table I). Lastly, different water-alcohol mixtures were studied; the results are listed in Table II.

As observed for the chloroform mixture, water is always the selectively pervaporated compound, and the azeotropic composition is not an obstacle to a complete purification of the alcohols. On the other hand, the selectivity is not affected by the lower boiling point of alcohols.

However, the interpretation of the transport selectivity in terms of selective interactions between diffusing species and polymer membrane is more complicated. Here, as in the case of water, alcohols are proton donors and highly self-associated. Moreover, in the case of PTFE-P4VP membranes, the comparison between chloroform-hydrocarbon and water-alcohol mixtures shows that the selectively pervaporated compound is a P4VP solvent



Mixture	Membrane	Temperature	Characteristic factors
A: Water (4 ml)	PTFE-P4VP 200% grafting	60°C	$\phi = 0.80$ l./hr m ²
B: Ethanol (96 ml)	PTFE thickness: 55 μ area: 20 cm ²		$\alpha = 6.6$

Fig. 6. Pervaporation graphical representation.

TABLE I
Pervaporation of a Water-Ethanol Azeotropic Mixture Through Different Membranes

		PTFE-P4VP, 200% grafting 82 μ^a	PTFE-PVP, 65% grafting 62 μ	Cellulose 75 μ	Cellulose acetate 100 μ	Cupro- phane 15 μ
20°C	ϕ , l./hr m ²	0.43	1.2	0.11	0.20	0
	α	6.6	6	6.2	5.9	
55°C	ϕ , l./hr m ²	0.80	2.03		0.29	0
	α	6.6	6		3	

* Dry membrane thickness.

in the former case (chloroform) and a P4VP precipitant in the latter (water). It becomes obvious that interpretation in terms of solvation effects only is not sufficient.

TABLE II
Pervaporation of Water-Alcohol Mixtures Through PTFE-P4VP Membrane^a

Grafting, %	Mixture	Initial composition	ϕ , l./hr m ²	α
50	water	20 ml	0.77	4.3
	isopropanol	80 ml		
50	water	10 ml	1.9	1.9
	ethanol	90 ml		
100	water	10 ml	2.1	2.1
	ethanol	90 ml		
160	water	10 ml	5.5	1.5
	methanol	90 ml		

^a PTFE thickness: 17 μ ; area: 20 cm²; temperature, 20°C.

The results listed in Table I show that the membranes which carry the most selective active groups (PTFE-P4VP and PTFE-PVP) allow a faster rate of pervaporation with about the same selectivity as the commercial membranes studied. This difference between the rate seems to be greater as the temperature increases. On the other hand, it was found that the temperature did not affect the selectivity of modified PTFE membranes (Table I).

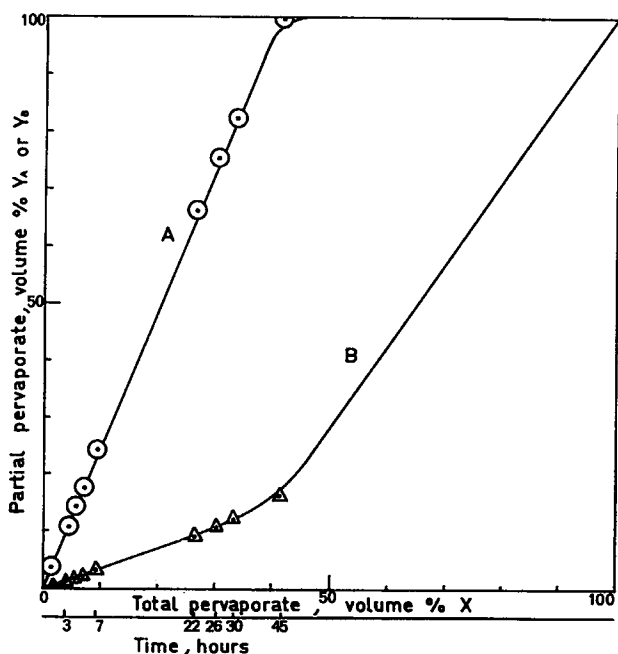
Water-Nucleophilic Solvents

In the following tests, the compounds mixed with water were always basic, i.e., hydrogen-bond acceptors. Some of them are of great industrial value because of the technical or economic disadvantages of existing methods for the total extraction of water.

For theoretical purposes, a great number of various bases were chosen, including amides, ethers, and sulfoxides. They boil at different temperatures: higher, similar, or lower than 100°C.

All the results are shown in Tables III and IV and in Figures 7-9. As already observed, water always pervaporates faster than the basic component even when the boiling point of the former is higher than that of the latter (water-tetrahydrofuran) or when the mixture is an azeotropic one (water-dioxane). In many cases, the selectivity was found to be very high and the rates good.

For instance (Figs. 7 and 8), with an initial mixture composed of 30 ml water and 70 ml dioxane or tetrahydrofuran, at 20°C, over a period of about 45 hr, 60 ml of pure dioxane or tetrahydrofuran was obtained. With the water-N,N-dimethylacetamide mixture (70 ml water, 30 ml DMA), the selectivity factor was infinite for a long time, so that 71 initial vol-% water was removed without DMA loss; but thereafter, selectivity rapidly decreased ($\alpha = 40$ for a mixture composition of about 30 vol-% water and $\alpha = 12$ for 20 vol-% water); and when the initial mixture contained 30 ml water and 70 ml DMA, only 15 ml of pure DMA was obtained. This means that inside a rich DMA mixture, water is eliminated with more diffi-

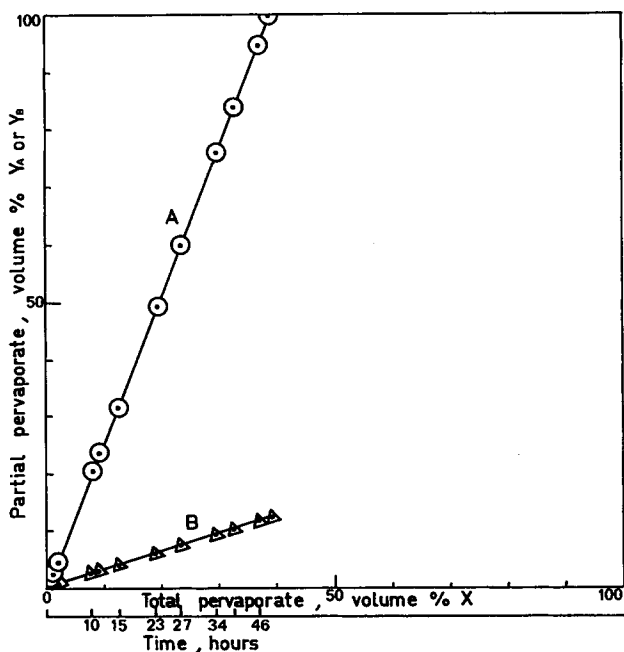


Mixture	Membrane	Temperature	Characteristic factors
A: Water (30 ml)	PTFE-PVP 65% grafting	25°C	$\phi = 0.70$ l./hr m ²
B: Tetrahydrofuran (70 ml)	PTFE thickness: 55 μ area: 20 cm ²		$\alpha = 8.5$

Fig. 7. Pervaporation graphical representation.

culty than inside a rich dioxane or tetrahydrofuran mixture. Water-N,N-dimethylformamide mixtures present the same characteristics as water-DMA. This trend may be explained by the fact that the total dehydration of these amides cannot easily be achieved by known techniques. As shown, it is possible to dehydrate such mixtures by pervaporation even at low temperature, and this is desirable for temperature-sensitive compounds. Pervaporation may be a simple inexpensive process adaptable for all types of dehydration so much more so as the modified PTFE membranes can be used for a long time without apparent high variation in their efficiency. A typical result with a PTFE-P4VP membrane/water-DMA mixture system is reported in Table V. It can be seen that after 4000 hr of continuous pervaporation, the rate and the selectivity of the fractionation remain almost constant.

However, an important disadvantage is the low pervaporation rate. But it can be seen (Tables III and IV) that temperature has no effect on selectivity, while it greatly increases pervaporation rate. On the other



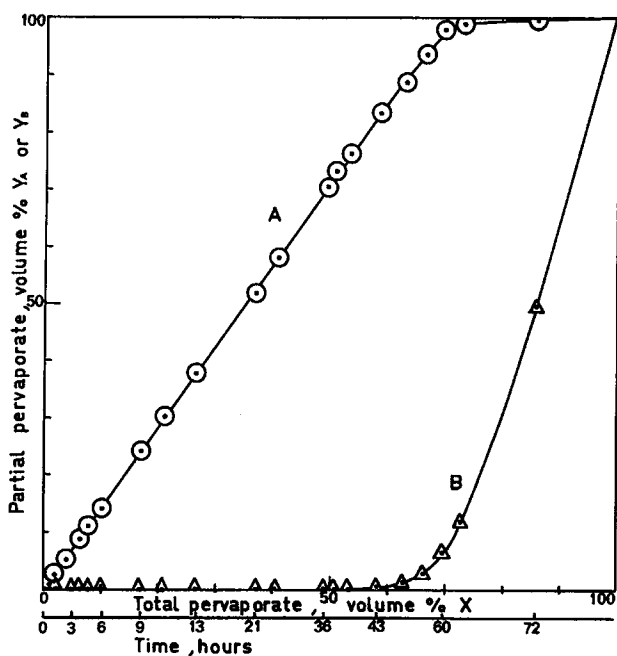
Mixture	Membrane	Temperature	Characteristic factors
A: Water (30 ml)	PTFE-PVP 65% grafting	20°C	$\phi = 0.44$ l./hr m ²
B: Dioxane (70 ml)	PTFE thickness: 55 μ area: 20 cm ²		$\alpha = 12$

Fig. 8. Pervaporation graphical representation.

hand, the thickness of the membrane is an important factor: when an asymmetrical PTFE-PVP membrane composed of a 3 μ dense skin and a 12 μ porous part is used, it was found that the pervaporation rate is about three times faster than with a dense membrane 55 μ in thickness, while the selectivity is only slightly lower or similar (Table VI).

These trends indicate that the pervaporation efficiency may be greater when either temperature increases or membrane thickness decreases.

The values listed in Tables II and III, referring to two PTFE-type membranes, may be qualitatively compared in spite of the very different grafting ratio in the two cases. They show that pervaporation rate and selectivity are about the same for any mixture. Because the per cent of grafting is smaller for PTFE-PVP membranes (65%) than for PTFE-P4VP (20%), the former seem to be more efficient. This result can be explained in terms of interactions, and it would appear that PVP has a greater tendency for H bonding than P4VP. In the PTFE-PVP membrane, both compounds, water and nucleophilic compound, exert a high solvating effect.



Mixture	Membrane	Temperature	Characteristic factors
A: Water (70 ml)	PTFE-P4VP 200% grafting	60°C	$\phi = 1.0 \text{ l./hr m}^2$
B: N,N-Dimethylacetamide (30 ml)	PTFE thickness: 55 μ area: 20 cm^2		$\alpha = \infty$

Fig. 9. Pervaporation graphical representation.

TABLE III
Pervaporation of Water-Nucleophilic Solvent Mixtures
Through PTFE-P4VP Membrane^a

Mixture		Boiling temp. of B, °C	Initial volume composition	Temp., °C	ϕ , l./hr m ²	α
A	B					
Water	Sulfolane	285	50/50	20	0.28	250
Water	Formamide	210	50/50	60	0.65	250
Water	Dimethylsulfoxide	189	50/50	20	0.36	300
Water	N,N-Dimethylacetamide	164	70/30	60	0.21	24
Water	N,N-Dimethylformamide	153	50/50	20	0.45	∞
Water			30/70	55	1.0	∞
Water	Dioxane	101	30/70	25	0.35	45
Water	Tetrahydrofuran	66	50/50	20	0.53	19
				20	0.77	5.5
				20		3

^a PTFE thickness: 55 μ , area: 20 cm^2 ; 200% grafting.

TABLE IV
Pervaporation of Water-Nucleophilic Solvent Mixtures
Through PTFE-PVP Membrane^a

Mixture		Boiling temp. of B, °C	Initial volume composition	Temp., °C	ϕ , l./hr m ²	α
A	B					
Water	Formamide	210	50/50	55	0.60	500
Water	N,N-Dimethyl- acetamide	164	70/30	20	0.27	200
Water	N,N-Dimethyl- formamide	153	50/50	20	1.57	200
			30/70	20	0.22	16
Water	Dioxane	101	30/70	20	0.44	12
				55	1.00	12
Water	Tetrahydrofuran	66	30/70	25	0.70	8.5

^a PTFE thickness: 55 μ area: 20 cm²; 65% grafting.

TABLE V
Effect of Pervaporation Time on Characteristic Factors^a

Pervaporation time, hr	0	1000	3000	4000
ϕ , l./hr m ²	0.21	0.21	0.22	0.25
DMA in pervaporate, vol-%	0	0	1	2

^a Mixture: water (70 ml)-N,N-dimethylacetamide (30 ml); membrane:PTFE-P4VP 200% grafting; PTFE thickness: 55 μ ; area: 20 cm².

TABLE VI
Effect of the PTFE-PVP Membrane Structure on Characteristic Factors

Membrane	Water, 4 ml Ethanol, 96 ml			Water, 50 ml N,N-Dimethylformamide, 50 ml		
	θ , °C	ϕ , l./hr m ²	α	θ , °C	ϕ , l./hr m ²	α
Homogeneous PTFE-PVP, 65% grafting; 55 μ thickness	20	1.2	6	20	0.58	21
	55	2.0	6			
Asymmetric PTFE-PVP; 74% grafting; 3 μ dense skin; 12 μ porous coat	20	3.5	6	20	1.6	15
	55	11.5	6			

In contrast, water has no solvating effect on the 4VP nonionic groups. In both cases, however, water has a larger diffusivity than the solvating basic solvent. As a consequence, as observed with water-alcohol mixtures, this selectivity transport cannot be explained in terms of nonspecific interactions (solvating effects) only, but must be expressed by introducing more specific interactions, such as hydrogen bonding in the present case.

CONCLUSIONS

In the various mixtures studied, it has been seen that there are complex interactions between diffusing species and active VP or 4VP units carried on the PTFE backbone. These interactions tend to increase pervaporation rates of the compound which has the higher probability of bonding with the membrane material.

The present paper does not purport to explain the pervaporation mechanism. Systematic studies would require detailed experiments to specify all factors affecting transport efficiency. Such investigations will form the subject of separated papers.

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